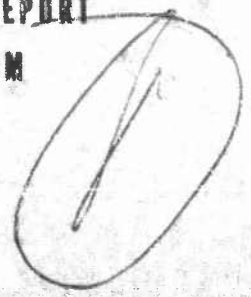


AD 666753

AD

TECHNICAL REPORT

67-77-CM

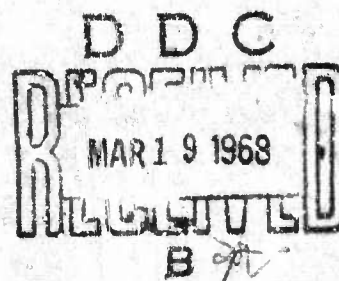


STUDIES ON THE STRUCTURE OF RUBBERY POLYURETHANES

This document has been removed
for public release and sale; its
distribution is unlimited.

by

S. B. Clough and N. S. Schneider



June 1967

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760



Clothing and Organic Materials Division

MR&E-67-2

Distribution of this
document is unlimited

AD _____

TECHNICAL REPORT
67-77-CM

STUDIES ON THE STRUCTURE OF
RUBBERY POLYURETHANES

by

S.B. Clough and N.S. Schneider
Materials Research Branch

Project Reference:
1C024401A329

Series: MR&E-67-2

June 1967

Clothing and Organic Materials Division
U.S. ARMY NATICK LABORATORIES
Natick, Massachusetts 01760

FOREWORD

This report summarizes certain results obtained from the initial phase of studies on the structure and properties of a series of elastomeric polyurethanes. The work was originally undertaken to obtain information needed for the interpretation of the water vapor permeability behavior of polyurethane films. However, the results proved to have much wider significance. Of particular interest are the discovery of a previously unreported transition not far above the temperature range of common usage, and the preliminary observations on light scattering and crystallization behavior which are important to an understanding of the mechanical and thermal behavior of polyurethanes. It is expected that later results from this program will lead to a model for the structural organization of polyurethanes that is able to account for the unusual properties of this important class of polymeric materials.

It is a pleasure to acknowledge the assistance of Mr. Kenneth Pigott of the Mobay Chemical Company in providing the structurally controlled polyurethane samples and many helpful discussions of the results. Contributions to the experimental results reported were made by Daniel Kisha, Bonita Mollicone and Abram King.

S. J. KENNEDY
Director
Clothing & Organic Materials Division

APPROVED:

DALE H. SIELING, Ph.D.
Scientific Director

W. M. MANTZ
Brigadier General, U.S.A.
Commanding

CONTENTS

	<u>Page</u>
List of Tables	v
List of Figures	v
Abstract	vi
1. Introduction	1
2. Experimental	2-3
a. Samples	2
b. Thermomechanical Analyzer (TMA)	2-3
c. Differential Scanning Colorimetry (DSC)	3
d. Light Scattering	3
e. X-ray	3
3. Results	4-6
a. Scanning Thermal Methods	4-5
b. Light Scattering	5-6
c. X-ray Diffraction	6
4. Discussion	7-12
5. Summary	13
6. References	14-15

LIST OF TABLES

<u>Title</u>	<u>Page</u>
I. Urethane Elastomer Transitions	16

LIST OF FIGURES

<u>Title</u>	<u>Page</u>
1. Typical TMA scan results for four polyurethane elastomers.	17
2. Typical DSC scan results for two Mobay polyurethane elastomers.	18
3. Intensity of scattered light vs. scattering angle for PTMG polyurethane film. Insert: I_H / I_V vs. scattering angle.	19

ABSTRACT

A variety of methods have been used to obtain information about the structural organization and transitions in several polyester and polyether type polyurethanes in order to gain a better understanding of the factors which control the mechanical behavior and water vapor transmission of this important class of polymers. Thermal scanning methods reveal three characteristic transitions which are common to all samples. The low temperature transition is the major glass transition. An intermediate transition in the range of 60-80°C is ascribed to urethane to polyester or polyether hydrogen bonding while the highest transition at 130-150°C is attributed to interurethane bonding. A transition at 205°C, which occurs only in the polyether samples, coincides with the melting of birefringent regions and is believed due to urethane crystallites. Light scattering measurements on this turbid sample indicate the existence of a wide range of structural order. Although crystallinity is absent in the unoriented samples, there is x-ray evidence of the stress induced crystallization of polyether or polyester segments. It is concluded that segregation of prepolymer and urethane segments into domain-like structure occurs in both types of polymers, but to a higher degree in the polyether than in the polyester based polymers, possibly due to restrictions in the latter imposed by interactions of the urethane and ester groups.

STUDIES ON THE STRUCTURE OF RUBBERY POLYURETHANES

1. Introduction

Linear polyester and polyether polyurethane elastomers, based on aromatic diisocyanates and chain extended with low molecular weight diols, exhibit a number of properties distinct from those of conventional rubbers. Of particular importance, the modulus-temperature curves show two marked transitions, one occurring below room temperature and one well above 100°C ,¹ with unusually high modulus values (ca. 10^8 dyne/cm.²) between these temperatures. As a result, the polyurethanes are useful thermoplastic materials. The low temperature transition is related to the onset of rotation in the flexible polyester or polyether segments of these copolymers. The reversible elasticity, as well as the high modulus displayed over the extended rubbery plateau, have been ascribed to intermolecular hydrogen bonding and strong dipolar interactions. Dissociation of this secondary bonding is presumably responsible for the marked high temperature transition.

Recently, Cooper and Tobolsky² inferred from the shape of the modulus temperature curves and from plasticization experiments on polyester based elastomers that segregation of stiff and flexible units into domains occurs, similar to the behavior of styrene-isoprene block copolymers. From infra-red absorption studies on non-chain-extended elastomers Boyarchuk, et. al.³ concluded that such ordering exists in polyether based samples, but that the spatial distribution of the urethane group is essentially homogeneous in the polyester polyurethanes. In the present work, a preliminary examination of the transitions and structural ordering in both polyester and polyether based elastomers was made by rapid scanning thermal methods, light scattering, and x-ray diffraction. Direct evidence for the existence of structural ordering of the urethane blocks in the polyether based sample has been obtained. Further, other^{1,2} transitions, in addition to the two commonly observed, were found in the various samples. These are interpreted in terms of the presence and degree of domain structure, and of the melting of crystallites.

2. Experimental

a. Samples

Laboratory samples, kindly supplied by the Mobay Chemical Co., were prepared in a two-step process. Prepolymers were formed from poly(1,4-butylene adipate) (PBA) and poly (tetramethylene glycol) (PTMG), each of molecular weight 2,000 by capping with 3.2 moles of diphenylmethane diisocyanate (MDI) per mole of polyester or polyether. Chain extension was achieved by reaction with 2.0 moles of 1,4-butane diol. Stringent precautions were taken during preparation to maintain moisture levels below 0.05 per cent. Casting of sheets and in some cases compression molding was followed by a 16 hr. cure at 100°C. Despite the curing step, these samples were soluble in dimethyl acetamide. (An unidentified fraction of less than 0.5 per cent from the PTMG based elastomer remained insoluble.) An uncured PTMG sample of the same formulation as above prepared by the one-step method where the three reactants were mixed simultaneously was also supplied. This sample was also soluble in DMA.

Commercial Estane samples (B.F. Goodrich Chemical Co.) of the same designation as the samples used by Cooper and Tobolsky are based on the same constituents as the Mobay polyester, but in different proportions. The polyester molecular weight is 800-1000⁴ lower than in the Mobay samples. The diisocyanate content for these samples is reported² as 38 per cent and 32 per cent in the 5707 and 5710, respectively, as compared to 27 percent in the Mobay samples. Both are soluble in tetrahydrofuran,⁵ and were supplied in pellet and sheet form.

b. Thermomechanical Analyzer (TMA)

In this accessory module of du Pont's DTA, a weighted probe is placed on the sample while it is heated at a programmed rate. The output trace, directly related to the probe position, reflects the combined effects of thermal expansion and probe penetration. Runs were made at heating rates of 5 - 10 deg./min. on samples of 0.05-0.10 inches in thickness. Different sensitivity settings and probe loads, typically 5 - 20 grams, were used to optimize the output in the various transition

regions. With constant sample thickness, load, and heating-rate the average deviation in the intersection of the extrapolated linear portions of the curves was usually less than 3°C. Increasing the load caused lowering of the intersection, thus the reported values of transition temperatures are indicative of a transition range.

c. Differential Scanning Colorimetry (DSC)

A Perkin Elmer DSC-1 proved useful in detecting heat capacity changes, though no absolute values could be obtained due to the lack of reproducibility of the slope of the output trace. Disks of the polyurethane films of about 15 20 mg. were dried at 50°C. in a vacuum oven for 16 hours before the runs were made at scanning rates of 10°C./min. The reported transition temperatures correspond to the peak values of the broad endotherms.

d. Light Scattering

Polarized high scattering measurements were performed on films of the turbid PTMG sample, by suitable modification of the beam geometry at the sample and detector on a Brice-Phoenix Model 2000 Photometer. With the sample normal to the incident beam, measurements ranged from scattering angles of 2.5 to 45 deg. with crossed (H_v) and parallel (V_v) polarizers. The high turbidity of the sample necessitated using thin (6 mil.) compression molded films. These were coated with microscope immersion fluid and supported between microscope cover slips.

e. X-ray

Flat plate x-ray diffraction photographs were produced using Ni filtered Cu radiation. Aluminum powder placed on the film surface aided in calculating lattice spacings. Measurements were made on the Mobay PTMG PBA samples at various elongations.

3. Results

a. Scanning Thermal Methods

Table I summarizes the results of these techniques by noting the positions of transitions in the temperature range from 100°C. to above 200°C. Figures 1 and 2 show typical curves obtained by these techniques. The DSC peaks have been adjusted to represent equal weight of the two samples. Of the various transitions, three appear to be common to all samples, but have varying definition in the output traces. The T_1 values obtained on the Estane samples compare well with the low temperature transitions estimated at 10°C. and 20°C. for the 5707 and 5710 samples, respectively, from the 10 sec. modulus-temperature curves of Cooper and Tobolsky.² However, there is no evidence in any of the previously reported mechanical behavior for the transition T_2 near the middle or upper end of the rubbery plateau which is revealed by the scanning thermal methods. T_2 is manifest as a diffuse endothermic peak in the DSC output trace, more marked in the case of the Mobay PBA sample than with the polyether. The corresponding TMA output indicated a limited increase in penetration in the T_2 region of these elastomers.

The TMA traces obtained in the present work show behavior in the temperature range above T_2 which closely resembles the modulus-temperature curves reported by Cooper and Tobolsky. The location of T_3 for the Mobay PBA elastomer coincides with the region of rapid modulus decrease reported¹ at 150 to 170°C. for such a system. In the case of Estane 5707 the correspondence of T_2 to the high temperature transition reported by Cooper and Tobolsky is also readily apparent. Their modulus temperature curve is linear over a 50 degree temperature range above t_g with some departure from linearity at about 100°C. leading to a tenfold drop in modulus through 150°C. With the Estane 5710 sample the major drop in modulus occurs above 100°C.² However, there is curvature in the modulus-temperature curve starting at $T=60^\circ\text{C}$. This temperature corresponds to the location of the T_2 transition determined for this sample in the present²

work. In correspondence with the modulus behavior, the penetration with TMA (Figure 1) was so great in the region just above T_2 , even with the smallest loadings which gave a steady response, that no evidence of a higher temperature transition could be obtained by this technique. The DSC trace for this sample showed a broad deviation from the baseline from the 80°C transition through 140°C.

In addition to these three common transitions, there are two others, specific to particular samples. In the Mobay PBA sample, TMA showed a 35°C. transition, while a relatively sharp endothermic peak at 205°C. was obtained by DSC with the PTMG elastomer. These transitions are evident in the curves of Figures 1 and 2 respectively.

b. Light Scattering

The PTMG based polyurethane samples were characteristically highly turbid. Since scrupulous attention was given to the exclusion of any moisture during the sample preparation, this turbidity is not the result of void formation. Further, the polyester based polymer prepared under identical conditions was optically clear. This indicates that the turbidity represents an inherent property of these polyether polyurethanes and provides direct evidence for the existence of inhomogeneities in density or in the orientation of optical anisotropy.

Partial analysis of the light scattering behavior from the PTMG based film of optical density $\tau_d = 0.2$ was performed to obtain information on the relative scattering contributions from density and orientation fluctuations. Fig. 3 shows the results of these light scattering measurements. Accurate correlation functions, derived by inversion of the intensity vs. scattering angle data, have not yet been obtained due to lack of data at angles large enough to perform the complete inversion. However, inspection of Fig. 3 shows that at low scattering angles corresponding to large distances in the film, the scattering is essentially isotropic ($I(H_\perp) \approx 0$) and therefore caused by density fluctuations. The correlation function for density fluctuations extends to distances approaching 1 micron.

At larger angles (smaller distances in the sample) H_V scattering becomes significant, increasing from 0.7 percent to 4.2 percent of the V_V intensity over the angular range of 5 to 45 degrees. This scattering is due to optically anisotropic elements, indicating the existence of regions of ordered structure which are of a size range that is much smaller than the density correlation distances.

c. X-ray Diffraction

No crystalline x-ray diffraction peaks could be obtained from unoriented films of either the polyester or polyether based samples. Studies at different elongations showed onset of crystalline peaks at extensions of 150 and 180 percent in the PBA and PTMG samples, respectively. The pattern from the polyether based elastomer at higher elongations showed one layer line and three equatorial peaks with spacings ($d = 4.41, 3.57, \text{ and } 2.34\text{\AA}$) which are close to those reported for high molecular weight poly(tetramethylene oxide) homopolymers.^{8,9} The polyester urethane at high elongations yielded one equatorial reflection and no layer line.

4. Discussion

T_1 is usually taken as the major glass transition^{1,2} related to onset of rotation about bonds in the flexible polyester and polyether chains. It has been determined in polyurethane elastomers by volume expansion¹⁰ as well as mechanical measurements.^{11,2} Recently, Miller¹¹ has suggested that the true glass transition actually occurs at a lower temperature, and that T_1 reflects a change from viscoelastic to elastomeric mechanical behavior.

In assigning mechanisms to T_2 and T_3 , a number of possibilities must be considered.² Saunders and Frisch¹ indicate that allophanate bonds, formed in the reaction of diisocyanate with urethanes, are relatively unstable, listing as evidence the fact that dissociation of these could be measured at temperatures of 106°C. and above. The cured Mobay samples with excess MDI would be expected to contain a significant amount of allophanate linkages, and even when stoichiometric amounts of reactants are used, allophanate formation is known to occur. On this basis, it appears useful to inquire whether T_3 might correspond to allophanate bond dissociation.

In reported data¹² on allophanate bond decomposition, the rate constant for the first order process¹¹ measured by infrared absorption, is 1.65×10^{-4} sec.⁻¹ at 150°C. Based on the time scale of the DSC experiment (scanning rates of 10°C/min.), assuming T_3 to be associated with a first order rate process, the rate constant would have to be an order of magnitude greater than the reported value if allophanate decomposition were the cause of this transition. Further, the solubility of the samples indicates that the concentration of allophanate groups must be small. Even the uncured Mobay PTMG sample, with presumably a lower concentration of allophanate linkages, showed a marked T_3 by both DSC and TMA. Thus it appears that T_3 can not be accounted for satisfactorily as due to allophanate bond decomposition.

The alternative view, that T_2 and T_3 be interpreted in terms of dissociation of intermolecular secondary bonding,¹³ seems preferable. Hydrogen bonding via the urethane N-H group will constitute the major contribution to these associations, but non-specific polar

interactions are also possible. There are two proton accepting groups available in each type of polyurethane: the urethane carbonyl or ester carbonyl in PBA samples, and the urethane carbonyl or ether oxygen in the PTMG elastomers. In an infra-red absorption study of H-bonding, Tanaka, et. al.¹⁴ studied N-H frequency shifts. They showed that virtually all N-H groups are in the H-bonded state, but they assumed that bonding occurs only with the appropriate oxygen atom in the polyester or polyether chain. Boyarchuk, et. al.³ studied the IR frequency shifts in the N-H absorption region of polyester based elastomers and in both the N-H and C=O regions of polyether polyurethanes. Although they agreed that the ester carbonyl provided the main contribution to H-bonding in polyester based samples, from the carbonyl shift they concluded that H-bonding is primarily between urethane groups in polyether samples. Accordingly, they pictured that the polyether sample was organized into domains of urethane groups dispersed in the polyether matrix, attributing the low concentration of urethane-ether H-bonding to steric hinderance. Such an inhomogeneous segregation of urethane groups throughout the sample is similar to that suggested by Cooper and Tobolsky² for polyester based elastomers. It should be noted that it was not possible for Boyarchuk to measure the urethane carbonyl absorption in the ester polyurethanes because of the presence of ester carbonyl.

It is our view that in polyester as well as in the polyether polyurethanes, H-bonding occurs both between the urethane segments themselves and between the urethanes and ether or ester segments of the molecule. The degree of each type will depend upon the composition as well as the processing conditions of the sample. We attribute T_2 to the dissociation of urethane-ester or urethane-ether H-bonding, whereas T_3 is believed due to dissociation of the urethane domains. The invariance of T_2 observed in Table I appears to be due to the similar strengths of H-bonding to the ether and ester functional groups, as shown by Boyarchuk in measurements on model compounds. The higher temperature of dissociation of strong inter-urethane H-bonding, corresponding to T_3 , presumably results from the stiffness and packing of

the urethane segments. ¹³ Such strong h-bond interaction was postulated by Kinko ¹³ between urethane segments in pseudo-crystalline regions of segmented polyether polyurethane fibers, similar to the H-bonding in polyamids.

Our interpretation of T_2 and T_3 is based on the following evidence. T_3 is sharper and much more pronounced in the PTMG sample, ³ where the degree of interurethane bonding is greatest. (Discussion below indicates that such association can lead to urethane crystallites in the polyether sample.) In contrast, T_2 is sharper and more pronounced in the polyester sample, where urethane-ester bonding predominates. Thus the occurrence of a T_3 as well as a T_2 transition in three of the polymer samples in Table I indicates that domain structure as well as distributed urethane-ester or -ether hydrogen bonding is present in these samples.

With this model it is possible to explain some disconcerting results of Tanaka. ¹⁴ In IR studies of the temperature dependence of hydrogen bonding on a polyester based system, he found very little decrease in the hydrogen bonding at temperatures up to 100°C. Correspondingly, the calculated energy of H-bond formation was 0.7 kcal./mol., which is exceedingly small. If one assumed that only a fraction of the total number of H-bonds were made to ester segments, the rest being the more stable interurethane type, then only the first type would dissociate at temperatures up to 100°C. Calculation of the equilibrium constant including correction for the fraction of urethane-urethane bonding would lead to a higher, more reasonable value of free energy.

The present interpretation of the T_2 and T_3 transitions is also useful in explaining the difference in the modulus temperature behavior observed for various polyester based samples. The Estanes are prepared from relatively low molecular weight polyesters (800-1000) as compared to the 2,000 molecular weight prepolymers used in the Mobay sample. Based on the percent composition, the Estane 5710 sample has a 2:1 molar ratio of diisocyanate to polyester, while in the Estane 5707 and Mobay PBA the ratio is very close to 3:1. The latter polymers have larger urethane segments corresponding stoichiometrically to two residues of butane diol and three of diisocyanate between

prepolymer chains. These larger urethane segments lead to better organized and more stable domains which are manifest by the T_3 transition apparent in the thermal methods, and by the high modulus at temperatures above T_2 . The smaller size of the urethane segments in Estane 5710 results in a lower proportion and reduced stability of the urethane domains. This is marked by the constantly decreasing modulus above T_2 and the lack of a perceptible T_3 transition. If the ratio were 1:1, such that the "hard segment" consisted merely of one diisocyanate molecule, one would not expect appreciable strength above T_2 . In fact, Colodny and Tobolsky¹⁸ found that such an elastomer flowed at 100°C.

We return to consider the two transitions which are not common to both the polyester and polyether based samples. The transition at 35°C. in the Mobay PBA sample is believed due to melting of crystallites of the polyester. Elastomers prepared from higher molecular weight polyesters are known to crystallize on storage.¹ The melting temperature of PBA homopolymer is 65°C.¹⁹ The displacement to a lower temperature might be due to the low molecular weight and the constraints on crystallite size and perfection caused by presence of the urethane segments.

The DSC endotherm at 205°C. in the Mobay polyether can definitely be identified with spherulites 6-8 μ in diameter which were observed in compression molded films of the uncured one-step sample. These melted on a kofler hot stage at about 207°C., in agreement with the peak on the DSC trace. The expected region for melting of crystallites of the polyurethane prepared from MDI and butane diol is 200°C. to 300°C.¹⁸ From the DSC endotherm it was estimated that on the order of 10 percent of the urethane segments had crystallized, representing only about 3 percent of the total polymer weight. The DSC endotherm from the sample prepared by the two-step process from the ether prepolymer indicated about the same order of crystallinity, though no structure was observable with the optical microscope.

In PTMG elastomers prepared by both techniques, a distribution in urethane segment lengths exists. Since the long segments would crystallize more readily, the difference between these two samples is probably due to the longer urethane segments in the samples prepared by the one-step technique which allows crystallization into recognizable spherulitic structures.

The crystallization of the longer urethane segments in the PTMC polymer is in keeping with the conclusion of Boyarchuk that a greater heterogeneity exists in the spatial distribution of urethane segments in the polyether based samples than in the polyester based elastomers.

The greater contribution to the light scattered by the turbid PTMC sample is from density fluctuations apparently associated with the small amount of urethane crystallinity. Qualitative observations indicate that the greatest decrease in turbidity as a function of temperature occurs just above 200°C. From the size of the calculated correlation function for density fluctuations we believe the V_v scattering arises from crystalline aggregates similar to the spherulites observed in the compression molded samples. That these aggregates are highly disordered is apparent from the very low value of H_v scattering. In well-ordered spherulitic structures such as polyethylene, the H_v scattering intensity is about 2/3 the V_v value. Even in rather disordered structures such as quenched polypropylene, the ratio of H_v to V_v scattering is approximately 1/3. In the present case this ratio is merely a few percent.

The increasing H_v component at the larger angles could arise from short range orientation correlation of either the crystallites or the non-crystalline domains. Both could have the optical anisotropy necessary to cause H_v scattering. Further measurements of the temperature dependence of scattered light would aid in determining the origin of this contribution to total scattering. Also, low angle x-ray scattering measurements are planned in order to study structural ordering in the hundreds of Angstroms range.

Whatever the detailed interpretation of the scattering behavior, the presence of crystalline urethane regions in the polyether based polyurethanes is direct evidence that a segregation of the urethane and prepolymer segments can occur. It seems reasonable to suggest that the observed spherulitic structures represent only one extreme of organization and that a wide range of urethane domain size and perfection occurs, much of it on a scale that does not contribute to light scattering. However, the larger end of the range of sizes contributes to the aspects of scattering behavior commented on above. The

presence of the crystalline urethane regions only in the polyether based samples supports the conclusion of Boyarchuk, et. al., that a greater segregation of urethane groups occurs in the polyether than in the polyester based elastomers.

The satisfactory comparison of the PTMG x-ray reflections with those of the pure homopolymer indicates that it is the flexible segment which crystallizes upon straining the sample. Rinke¹⁵ assumed the diffraction to be due to pseudocrystalline urethane regions in a stretched polyether polyurethane. The relatively low elongations at which crystallite diffraction was observed in the present study reflects the high degree of chain orientation, caused by the intermolecular bonds acting as crosslinks.

5. Summary

The measurement of transition temperatures and the analysis of optical behavior has provided further information about the interactions and structural organization of elastomeric polyurethanes, and the effect of these factors on mechanical behavior. Two separate transitions have been identified and interpreted in terms of H-bonding, and indicate that two distinct types of H-bonding exist in all the polyurethanes studied in this work. The T_2 transition occurring at 80°C involves H-bonding between the urethane secondary amine group and the ester carbonyl or ether oxygen of the prepolymer, while the T_3 transition occurring at about 140°C or above is ascribed to interurethane H-bonding. The presence of interurethane H-bonding which dissociates at higher temperatures than the urethane-prepolymer type is connected with the segregation of urethane groups leading to domain structure. There is evidence of several types that the extent of interurethane bonding and domain structure is greater in the polyether than the polyester polyurethanes. It appears that the greater amount of H-bonding between the urethane and the groups of the polyester chain gives rise to higher but more temperature dependent modulus values than in the equivalent polyether based elastomer. Greater hysteresis in the stress-strain curve might also be predicted for the polyester urethanes, but there is not adequate published information on this type of behavior. More extensive measurement of the temperature dependence of the polyurethane properties, including mechanical behavior, infra-red absorption and scattering in the optical and x-ray regions are required to provide further elucidation of the organization present in these elastomers.

6. References

1. Saunders, J. H., and K. C. Frisch, Polyurethanes: Chemistry and Technology, Interscience Publishers, New York (1962). Pt. 1.
2. Cooper, S. L. and A. V. Tobolsky, J. Appl. Polymer Sci., 10, 1837 (1966); Textile Research Journal, 36, 9 (1966).
3. Boyarchuk, Yu, M., L. Ya. Rappoport, V. N. Nikitin, and N. P. Apukhtina, Polymer Science USSR, 7, 859 (1965).
4. Schollenberger, C. S., Chem. Abstracts, 53, 7651b of U. S. patent 2,871,218.
5. Cooper, S. L., Viscoelastic Properties of Segmented Elastomers and High Temperature Polymers, Ph. D. Thesis, Princeton University (1966).
6. Stein, R. S., and J. J. Keane, J. Polymer Sci., 17, 21 (1955).
7. Stein R. S., and P. R. Wilson, J. Appl. Phys., 33, 1914 (1962).
8. Cesari, M., G. Perego, and A. Mazzei, Makromol. Chem., 83, 196 (1965).
9. Imada, K., T. Miyakawa, Y. Chatani, H. Tadokoro, and S. Murahashi, Makromol. Chem., 83, 113 (1965).
10. Smith, T. L., and A. B. Magnusson, J. Polymer Sci., 42, 391 (1960).
11. Miller, G., Polymer Preprints, 8, 1072 (1967).
12. Kogon, I. C., J. Org. Chem., 23, 1594 (1958).

13. Andrews, R. D., J. Polymer Sci., Pt. C, No. 14, 261 (1966).
14. Tanaka, T., T. Yokoyama, and K. Kaku, Men. Fac. Eng. Kyushu Univ., 23, (2), 113 (1963).
15. Rinke, H., Angew. Chem., 74, 612 (1962).
16. Colodny, P. C., and A. V. Tobolsky, J. Am. Chem. Soc., 79, 4320 (1957).
17. Morgan, P. W., Condensation Polymers: By Interfacial and Solution Methods, Interscience Publishers, New York (1965).
18. Ref. 1, Pt. II, p. 669 ff. gives melting points of polyurethanes of various composition.
19. Keijzers, A. E. M., J. J. van Aartsen, and W. Prins, J. Appl. Phys., 36, 2874 (1965).

TABLE I

URETHANE ELASTOMER TRANSITIONS

deg. C.

		T_1		T_2	T_3	
Mobay	PBA	TMA	-45	35	64	148
		DSC	-	-	80	167
Mobay	PTMO	TMA	-85		60	153
		DSC	-		80	153
Estane	5707	TMA	-12		60	130
		DSC	-		85	
Estane	5710	TMA	-18		60	
		DSC			83	

- Technique not used in this temperature range.

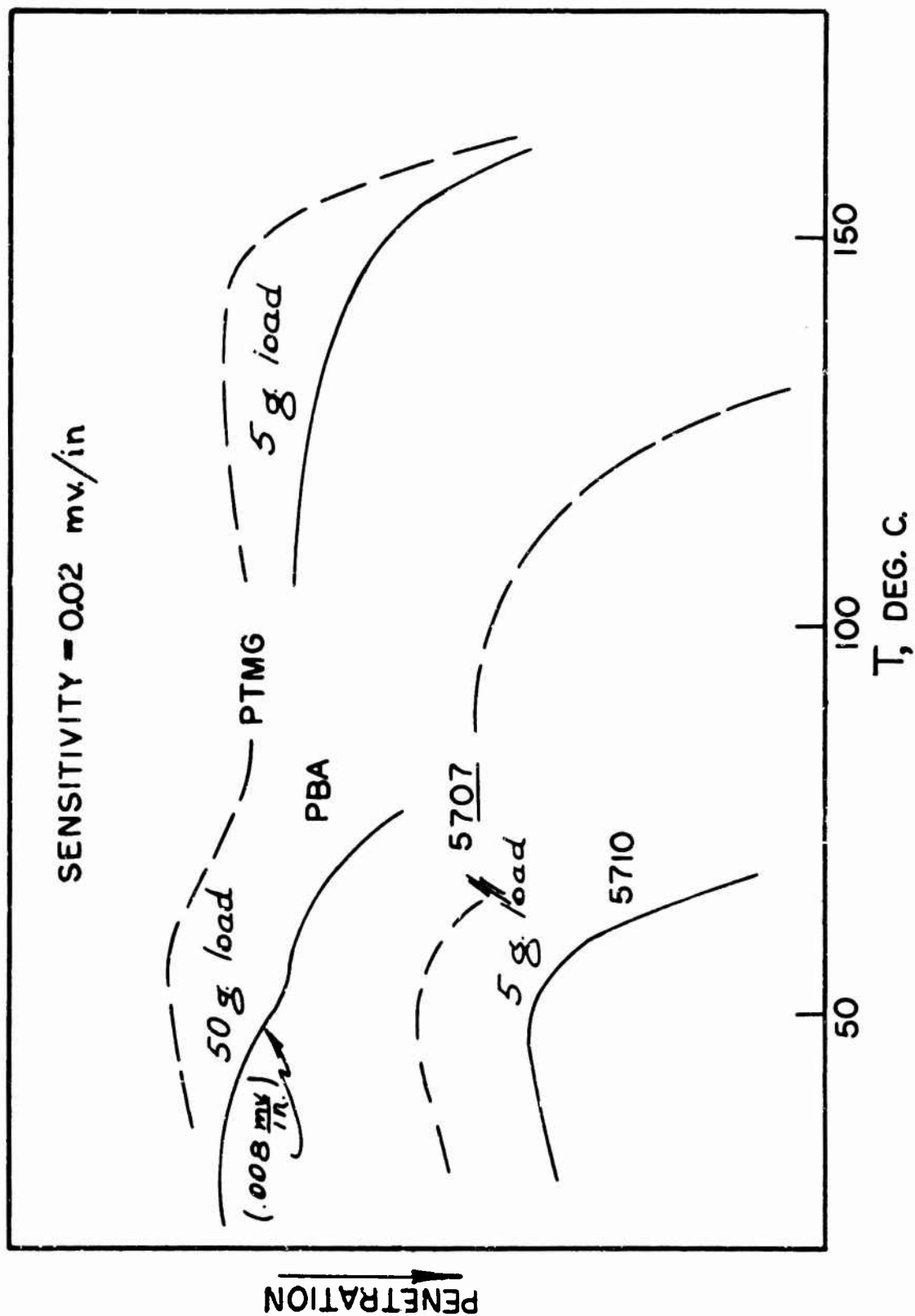


Figure 1. Typical TMA Scan Results for Four Polyurethane Elastomers.

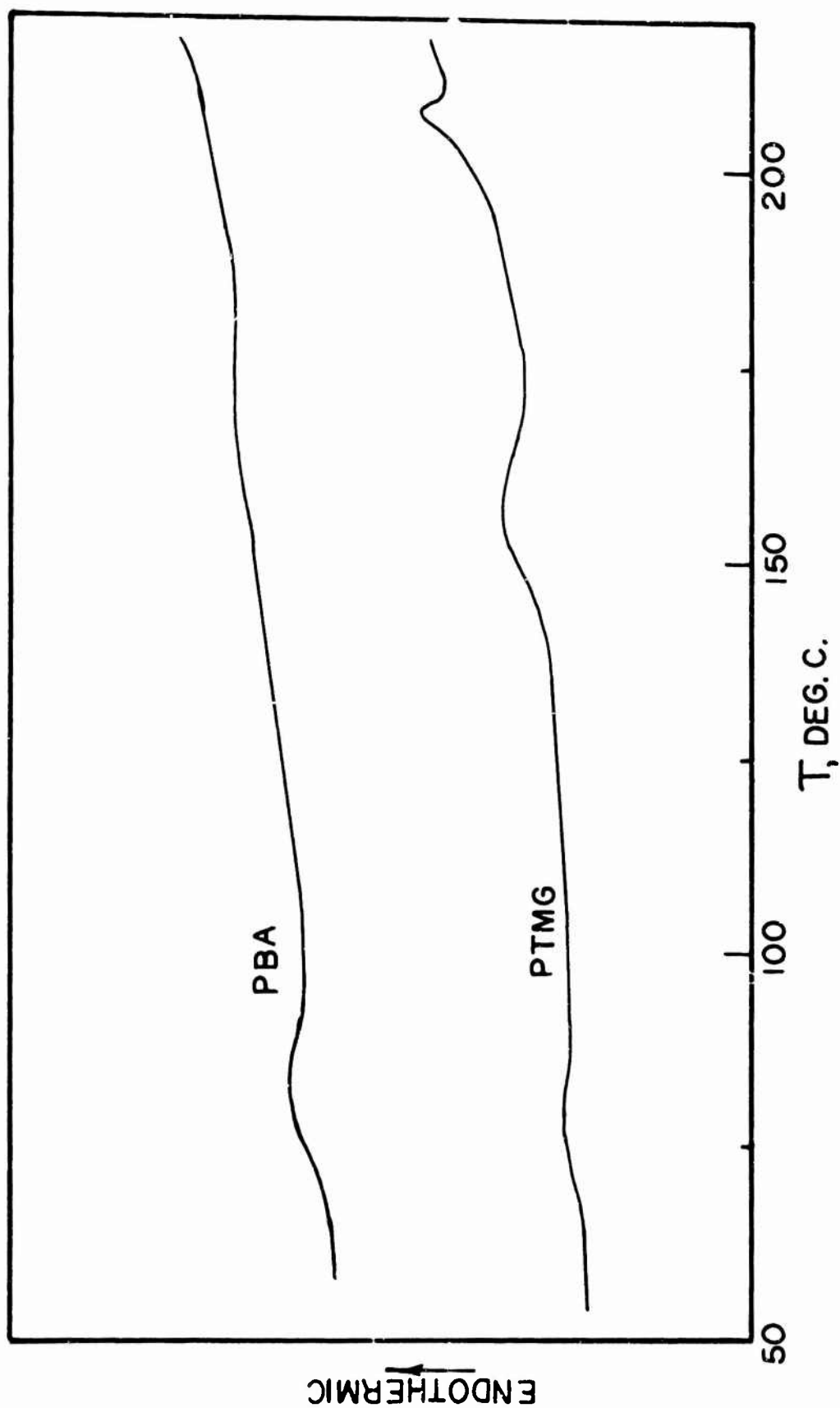


Figure 2. Typical DSC Scan Results for Two Mobay Polyurethane Elastomers.

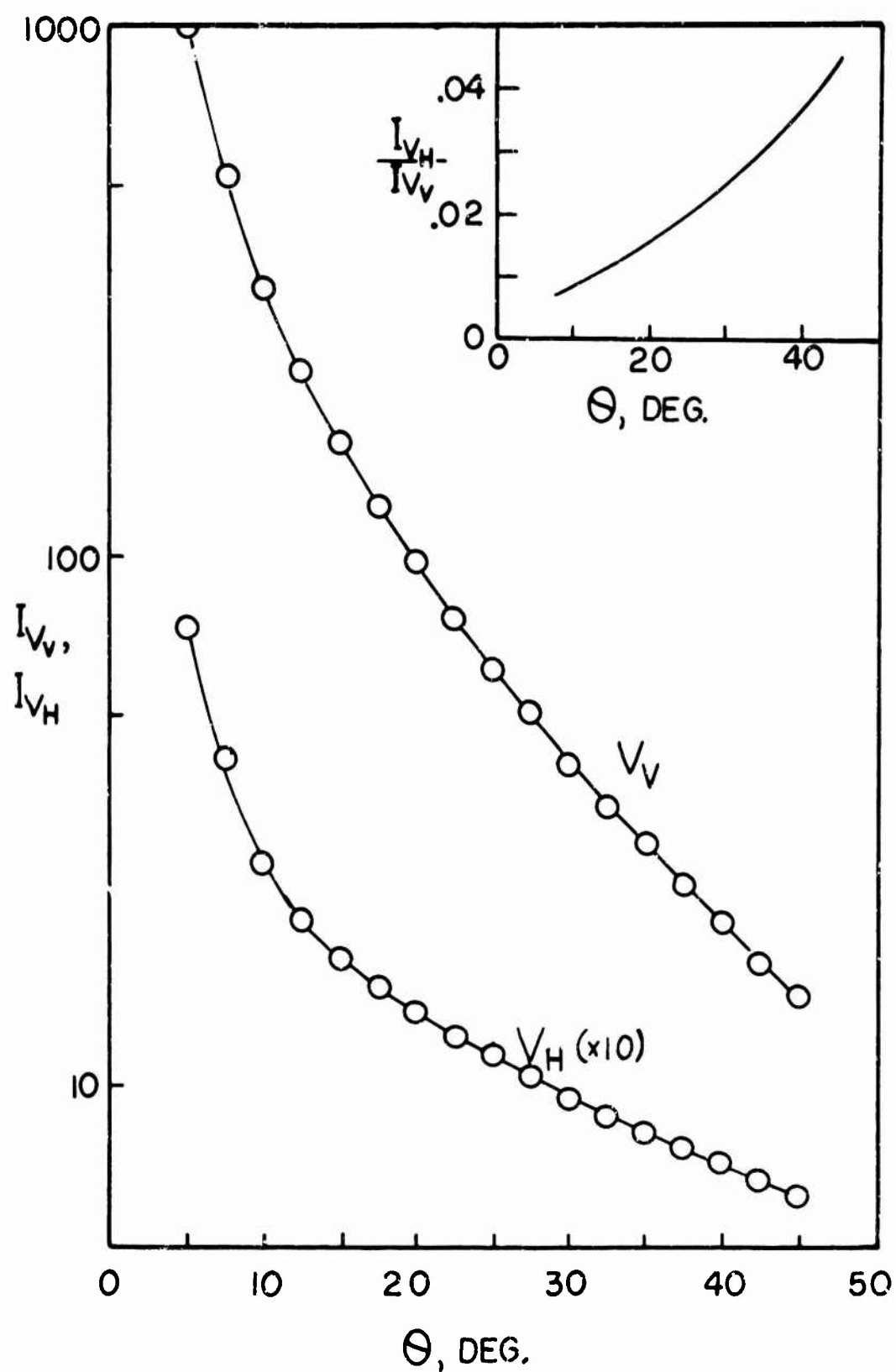


Figure 3. Intensity of Scattered Light vs. Scattering Angle for PTMG Polyurethane Film. Insert: I_{H_V}/I_{V_V} vs. Scattering Angle.

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) U. S. Army Natick Laboratories Natick, Massachusetts 01760		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
		2b. GROUP
3. REPORT TITLE STUDIES ON THE STRUCTURE OF RUBBERY POLYURETHANES		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Materials Research Jan. 1966- March 1967		
5. AUTHOR(S) (First name, middle initial, last name) Stuart b. Clough and Nathaniel S. Schneider		
6. REPORT DATE June 1967	7a. TOTAL NO. OF PAGES 19	7b. NO. OF REFS 19
8a. CONTRACT OR GRANT NO.	8b. ORIGINATOR'S REPORT NUMBER(S) 67-77-CM	
b. PROJECT NO. 1C024401A329		
c.	8b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.	MR&E-67-2	
10. DISTRIBUTION STATEMENT Distribution of this document is unlimited. Release by CFSTI is authorized.		
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY U.S. Army Natick Laboratories Natick, Massachusetts
13. ABSTRACT A variety of methods have been used to obtain information about the structural organization and transitions in several polyester and polyether type polyurethanes in order to gain a better understanding of the factors which control the mechanical behavior and water vapor transmission of this important class of polymers. Thermal scanning methods reveal three characteristic transitions which are common to all samples. The low temperature transition is the major glass transition. An intermediate transition in the range of 60-80°C is ascribed to urethane to polyester or polyether hydrogen bonding while the highest transition at 130-150°C is attributed to interurethane bonding. A transition at 205°C, which occurs only in the polyether samples, coincides with the melting of birefringent regions and is believed due to urethane crystallites. Light scattering measurements on this turbid sample indicate the existence of a wide range of structural order. Although crystallinity is absent in the unoriented samples, there is x-ray evidence of the stress induced crystallization of polyether or polyester segments. It is concluded that segregation of prepolymer and urethane segments into domain-like structure occurs in both types of polymers, but to a higher degree in the polyether than in the polyester based polymers, possibly due to restrictions in the latter imposed by interactions of the urethane and ester groups.		

DD FORM 1473

REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

UNCLASSIFIED

Security Classification

UNCLASSIFIED
Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Structure	8					
Mechanical properties	8		7			
Molecular properties	8		7			
Permeability	8		7			
Temperature	8		6			
Polyurethane resins	8,9		9			
Rubbery	0					
Copolymers	9					
Segmented	0					
Calorimeters	10					
Thermomechanical analyzer (TMA)	10					

UNCLASSIFIED

Security Classification